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MANY ELECTRON EFFECTS IN THE PHOTOELECTRON SPECTRA OF  
CONDENSED NITRIC OXIDE(U) PENNSYLVANIA UNIV

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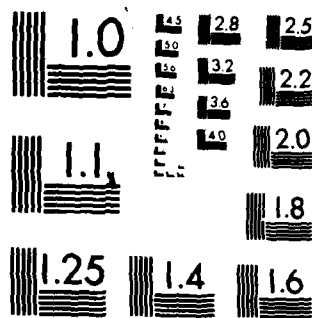
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from an intermolecular charge transfer from one NO monomer to the other, while the second peak arises from intramolecular screening. The first two peaks in the valence region, which have the smallest binding energies and are separated by 2.6 eV, arise from final states which have  $^2A_1$  and  $^2B_2$  symmetries, respectively. The  $2\pi$  orbitals of the monomers combine in-phase and out-of-phase to form  $a_1$  and  $b_2$  orbitals of the dimer. The resulting two final states of the dimer depend upon which orbital is occupied by the unpaired electron.

1. . B.P. Tonner, F. Greuter, E.W. Plummer and W.R. Salaneck, to be published.

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# Many-Electron Effects in the Photoelectron Spectra of Condensed Nitric Oxide

C.M. Kao

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

T.C. Caves

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

R.P. Messmer

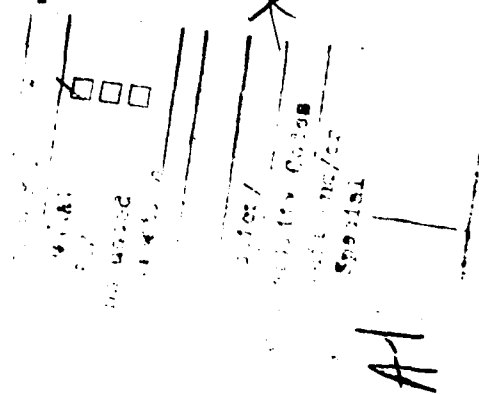
General Electric Corporate Research and Development, Schenectady, New York 12301 and Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

$\pi$  Superscript 2 A Subscript 1 Superscript 2 B Subscript 2

The valence and core level photoelectron spectra of NO condensed on various substrates as obtained by Tonner et al. can be successfully explained using an NO dimer model in which the two NO molecules form a weak N-N bond via the  $2\pi$  orbitals of the monomers, resulting in a nearly square geometry. In both the O(1s) and N(1s) regions of the x-ray spectrum there are two intense peaks separated by 3.4 eV. From generalized-valence-bond calculations we find for the N(1s) case, that the peak with the smaller electron binding energy arises from an intermolecular charge transfer from one NO monomer to the other, while the second peak arises from intramolecular screening. The first two peaks in the valence region, which have the smallest binding energies and are separated by 2.6 eV, arise from final states which have  $^2A_1$  and  $^2B_2$  symmetries, respectively. The  $2\pi$  orbitals of the monomers combine in-phase and out-of-phase to form  $a_1$  and  $b_2$  orbitals of the dimer. The resulting two final states of the dimer depend upon which orbital is occupied by the unpaired electron.

a Subscript 1 b Subscript 2

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## I. INTRODUCTION

Satellite structures are observed in an increasing number of photoelectron spectra (PES) and arise from electron correlation effects not strictly describable in the molecular-orbital approximation. The electron correlation effects responsible for satellite structures may arise in the final state (ion) or the initial state (neutral) or both. In this paper we will discuss the PES of condensed nitric oxide (NO) which interestingly demonstrates the effects of electron correlation in both the initial and the final states.

The experimental PES of condensed NO (10 K to 40 K) as obtained by Tonner *et al.*<sup>1</sup> for the valence region and the core regions of N(1s) and O(1s) are shown in Fig. 1a and 1b, respectively. The valence spectrum was obtained using synchrotron radiation monochromatized to 60 eV; for comparison, the gas phase data from an (e,2e) dipole coincident-electron experiment<sup>2</sup> at an effective "photon" energy of 60 eV are also included in Fig. 1a (solid line). Except for the additional peak VIS2, the solid phase spectrum in the valence region is very similar to the gas phase, aside from a uniform energy shift due to the extra relaxation present in the solid phase (note that different energy references are applied for the gas phase and the solid phase in Fig. 1a). Hence, in the valence region, we are mainly interested in the origin of peak VIS2, acknowledging the other features are easily explained as the ionization of  $2\pi$ ,  $5\sigma$  and  $1\pi$ , and  $4\sigma$  electrons (in order of increasing binding energies) from NO in both the solid phase and the gas phase. In the N(1s) and O(1s) core regions of the solid, one observes two peaks in each case separated by 3.4 eV. In contrast, the gas phase spectra have only one prominent peak in each region, with small shoulders (intensities  $\sim 1/3$  of main peak) due to exchange splittings<sup>3</sup> of 1.5 eV and 0.7 eV in N(1s) and O(1s), respectively.

The difference between the PES of condensed NO and that of gaseous NO is obviously due to the intermolecular interaction present in the condensed phase. It is well known that NO in the solid phase exists in dimeric form<sup>4</sup> and is diamagnetic.<sup>5</sup> This NO dimer has also been detected in the gas phase<sup>6</sup> and in low-temperature matrices.<sup>7</sup> It is weakly bound by  $\sim 1.7$  kcal/mole.<sup>8</sup> The structure of  $(\text{NO})_2$  has been determined by X-ray crystallography<sup>4</sup> and by gas-phase microwave studies<sup>6</sup> and may be characterized by a weak bond between the two nitrogens with  $R_{\text{NN}}=2.24\text{\AA}$ ,  $R_{\text{NO}}=1.16\text{\AA}$ , and  $\angle\text{NNO}=99.6^\circ$ . The weak binding in  $(\text{NO})_2$  is reflected in the structural observations that  $R_{\text{NO}}$  in  $(\text{NO})_2$  is about the same as in NO ( $1.15\text{\AA}$ ) and that the dimer has a very long N-N bond distance. However, as we shall see below, it is this weak bond that is crucial to understanding the PES of condensed NO.

Calculated results are based on correlated wavefunctions in the framework of generalized-valence-bond (GVB) theory.<sup>9</sup> The GVB wavefunctions, although correlated, retain a simple one-electron-like picture which offers a simple physical description of the electronic structure.

## II. CALCULATIONAL DETAILS

The most important solid-state effect on the PES of condensed NO is the intermolecular interaction within the NO dimer. To a good approximation, the polarization effects of the medium on different ion states may be regarded as a constant and hence they will not change the spectrum except for a shift in absolute energy. Therefore in our calculations we shall consider only an isolated NO dimer. The molecular structural data are taken from the work of Kukolich<sup>6</sup> on gaseous  $(\text{NO})_2$ , which are perhaps the most accurate at present and are very close to the earlier x-ray crystallographic data of Lipscomb;<sup>4</sup>

however, minor deviations of these geometrical parameters are not expected to change our description.

All electrons, except for the 1s cores, are correlated in terms of GVB pairs in most of our calculations. This results in eleven pairs for the dimer, as each NO monomer contributes five GVB pairs (one  $\sigma$  bond, one  $\pi$  bond, two oxygen lone pairs, and one nitrogen lone pair), and there is one pair describing the N-N bond. The effect of electronic correlation in describing the long N-N bond is crucial, and its neglect is the reason for the failure of Hartree-Fock theory in predicting the bond length (the N-N bond length is too short by  $\sim 0.6\text{\AA}$ ).<sup>10</sup> Inclusion of the other GVB pairs, although not as important, is very helpful in revealing the physics of the electronic structure.

Calculations were done using the GVE2P5 program,<sup>9</sup> with double-zeta basis sets plus d polarization functions (exponents of 0.76 and 0.85 for nitrogen and oxygen, respectively) of Dunning and Hay.<sup>11</sup>

### III. RESULTS AND DISCUSSION

The ground state NO dimer is calculated to be slightly unbound by 1.6 kcal/mole with respect to two NO molecules (at the experimental bond distance of 1.15Å).<sup>12</sup> It should be noted however, that the experimental binding energy of  $(\text{NO})_2$  is only 1.7 kcal/mole. Optimization of the geometries and the inclusion of higher level correlation effects should bring the calculated binding energy closer to experiment. The discrepancy is not critical here, however, because the separations in the PES peaks which we wish to describe are of the order of 3 eV (1 eV=23.06 kcal/mole).



In the following, we shall describe the ion states responsible for the PES of  $(\text{NO})_2$  by considering the ionization energies and the relative intensities.

#### A. Ionization Energies

First, consider the lowest  $\text{N}(1s)$  core hole state  $\text{NIS1}$ . The wavefunction is obtained in the presence of a localized core hole. This reduction in symmetry of the wavefunction for core hole states is not a serious problem (e.g., the splitting for the  $g$  and  $u$  core-hole states in  $\text{N}_2$  is less than 0.1 eV),<sup>13</sup> and yields much more accurate ionization energies than calculations based on symmetry orbitals.

The two GVB orbitals which form the weak  $\text{N-N}$  bond in the neutral ground state (GS) are shown in Fig. 2a; the bond is described by a valence-bond like wave function:  $(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha)$ . On ionization of a  $\text{N}(1s)$  electron, these orbitals become much like a lone pair localized on the nitrogen containing the core hole (the nitrogen on the left), as is clear in Fig. 2b. In fact, the monomer with the core hole effectively resembles an excited state of the  $\text{O}_2$  molecule, due to an intermolecular charge transfer from the other monomer which now resembles an  $\text{N}_2$  molecule in the valence region. Schematically, the GVB wavefunctions for GS and  $\text{NIS1}$  are shown in Fig. 3a and 3b, respectively, to illustrate the charge transfer (from right to left) and the electronic reorganization.

The second peak,  $\text{NIS2}$ , results from intramolecular screening (i.e., screening within the one  $\text{NO}$  molecule of the dimer which has the core hole localized on it). The GVB wavefunction for this intramolecularly screened

state is obtained by triplet coupling of the two orbitals originally forming the N-N bond (the wavefunction is still a doublet by properly coupling the N(1s) orbital). The energy splitting between NIS1 and NIS2 is calculated to be 3.7 eV, in comparison with the experimental 3.4 eV.

In the O(1s) region, the GVB wavefunction in the valence region for the lowest hole state OIS1 is quite different from that for NIS1. As shown in Fig. 2c, the two orbitals originally forming the N-N bond in the GS still retain this character and there is no intermolecular charge transfer of the kind encountered earlier in NIS1 (cf. Fig. 2b). The second peak, OIS2, like NIS2, is characterized as dominantly triplet-coupling of the two N 2 $\pi$  electrons originally involved in the N-N bond of (NO)<sub>2</sub>. The energy separation between OIS1 and OIS2 is obtained from a simple configuration-interaction (CI) calculation using three orbitals (O(1s) and N-N bond pair) of the OIS1 GVB wavefunction, and is found to be 3.3 eV, which may be compared with the experimental separation of 3.4 eV. Intermolecular charge transfer between the two O atoms does not occur in this case because the  $\pi$ -bond (perpendicular to the dimer plane) of the donor would have to be disrupted at great energy.

In the valence region, it is more convenient to use symmetry-restricted ( $C_{2v}$ ) wavefunctions. It turns out that the first two peaks (cf. Fig. 1a) are both derived from ionizations of an electron out of the N-N bond, with the remaining electron in a bonding  $a_1$  orbital for the main peak VIS1 ( $^2A_1$ ) and in an anti-bonding  $b_2$  orbital for the second peak VIS2 ( $^2B_2$ ). The energy separation between the  $^2A_1$  and the  $^2B_2$  ion states at this level of approximation is 2.7 eV, which may be compared with the experimental value of 2.6 eV.

## B. Intensities

The intensities of the PES peaks also contain valuable information on the wavefunctions of the ion states and the neutral parent. Thus far we have discussed the positions of the ionization peaks which are in reasonable agreement with experiment. However, our descriptions could not be considered correct if the relative intensities could not be accounted for. In the following, we shall provide qualitative arguments concerning the intensities in support of our description of the PES.

The relative intensity  $I_i/I_j$  of ion state  $i$  relative to ion state  $j$  in the sudden approximation<sup>14</sup> is

$$\frac{I_i}{I_j} = \frac{|\langle \Phi_i^+ | \hat{a}_i \Phi^0 \rangle|^2}{|\langle \Phi_j^+ | \hat{a}_j \Phi^0 \rangle|^2} \quad (1)$$

where  $\hat{a}_i$  and  $\hat{a}_j$  are the appropriate electron annihilation operators operating on the wavefunction  $\Phi^0$  of the neutral parent, and  $\Phi_i^+$  and  $\Phi_j^+$  are the calculated self-consistent wavefunctions of ion states  $i$  and  $j$ , respectively.

Instead of evaluating Eq. 1 rigorously using our calculated wavefunctions, we shall focus only on the few orbitals that change shape or spin coupling most drastically in the ion states, and thus assume all other orbitals have no effect in the overlap integral.

The two O(1s) ion states OIS1 and OIS2 differ mainly in the spin couplings of the two  $2\pi$ -like orbitals shown in Fig. 2c. In OIS1 they are predominantly singlet coupled and in OIS2 they are predominantly triplet coupled. The weights of singlet and triplet couplings in each state are easily obtained from the CI wavefunctions. Within the present approximation only singlet cou-

pling gives non-zero overlap with the GS. An intensity ratio of 0.05 is predicted for OIS2 relative to OIS1. The source of mixing between the singlet and triplet couplings in each state is the intramolecular coupling of the O(1s) and the  $2\pi$ -like orbitals.

The relative intensities for NIS1 and NIS2 may be understood similarly. However, as indicated in Fig. 3, there are drastic rearrangements of the orbitals between these two states. Therefore, the weights of the singlet and the triplet couplings involving the  $2\pi$ -like orbitals cannot be accurately determined from a small CI calculation using one common set of orbitals. Nonetheless, the intensity of NIS2 relative to NIS1 is expected to be larger than the intensity of OIS2 relative to OIS1 because the overlap between GS and the singlet coupled wavefunction NIS1 is smaller due to orbital rearrangements (cf. Fig. 3), and this "lost" intensity in NIS1 appears in NIS2.

In the valence region, we have assigned VIS1 and VIS2 as the  $^2A_1$  and the  $^2B_2$  ion states, respectively. The neutral ground state GS is  $^1A_1$ . In the molecular-orbital (MO) approximation, only the  $^2A_1$  state is expected if the NO dimer is bonded via an  $a_1$  orbital derived from the  $2\pi$  orbitals of the NO monomers. As mentioned earlier, the single-determinant MO wavefunction does not properly describe the long N-N bond. The GVB description for this bond, expressed in terms of MO's ( $a_1$  and  $b_2$ ), is

$$|\phi_1^N \phi_2^N(\alpha\beta - \beta\alpha)| = \lambda_1 |a_1 a_1 \alpha\beta| - \lambda_2 |b_2 b_2 \alpha\beta|, \quad (2)$$

where  $\lambda_1$  and  $\lambda_2$  are the occupation numbers for orbitals  $a_1$  and  $b_2$ , respectively. In the usual restricted Hartree-Fock method,  $\lambda_2$  is zero. The closer  $\lambda_2$  is to  $\lambda_1$ , the more biradical-like (non-bonding) the system is. It is clear from Eq. 2 that the occupation of the  $b_2$  N-N anti-bonding orbital in the GS is

the reason for the observation of VIS2. Namely, the intensity of  ${}^2B_2$  relative to  ${}^2A_1$  is  $(\lambda_2 / \lambda_1)^2$ , assuming the natural orbitals (NO's)  $a_1$  and  $b_2$  in the ion states and the neutral ground state are the same. The calculated values for  $\lambda_2$  and  $\lambda_1$  are 0.22 and 0.78 respectively, from which the intensity ratio of 0.13 is predicted, consistent with the experiment. The two-peak feature here is an example of both the initial-state and the final-state effects. Furthermore, VIS2 is broader because of the repulsive potential due to the occupation of the  $b_2$  anti-bonding orbital in the ion.

#### IV. SUMMARY

The experimental PES of solid NO in both the valence and core regions have been successfully explained here using an NO dimer model. The satellite structures are basically due to the presence of the weak N-N bond in the neutral dimer. In the valence region, the two peaks VIS1 and VIS2 both result from the ionization of an electron from the N-N bond. In the N(1s) region, NIS1 is characterized by intermolecular charge transfer which is absent in NIS2. The two peaks in the O(1s) region OIS1 and OIS2 also do not involve the intermolecular charge transfer. Their splitting is due primarily to spin-coupling effects.

The mechanism of intermolecular charge transfer is interesting and is expected to occur in other similar situations in which weak bond(s) may form between neighbors. Bonding is necessary for intensity reasons. But if the bond is very strong, then there is usually no satellite structure associated with it. A qualitative description of the energetics and intensity of this type of charge transfer has been given in the present paper. A more quantitative analysis will appear elsewhere.<sup>15</sup>

## V. ACKNOWLEDGMENTS

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# Figure Captions

## Figure 1

Photoelectron spectra of NO.<sup>1</sup> (a) Valence region at 60 eV photon energy. Solid phase (dashed line) is referenced to substrate Fermi energy; gas phase (solid line, from Ref. 2) is referenced to vacuum energy. (b) Oxygen 1s and Nitrogen 1s regions for solid NO on polycrystalline gold. Energies are relative to Au Fermi energy.

## Figure 2

GVB orbital contour plots of the  $2\pi$ -derived valence orbitals. (a) The two orbitals describing the N-N bond in the neutral ground state. (b) The two corresponding orbitals in the charge-transfer N(1s) ion state NIS1 showing intermolecular charge transfer to the left N atom where the core hole is localized. (c) The two corresponding orbitals in the O(1s) ion state OIS1.

## Figure 3

Schematic representations of the wave functions for (a) the neutral ground state of the NO dimer; (b) the charge-transfer N(1s) ion state NIS1, in which the core hole is localized on the left. The lines connecting pairs of orbitals represent bonds between these orbitals. The single segment lines represent  $\sigma$ -bonds (and in the case of the monomer on the right in (b)-- a  $\pi$ -bond); the three-segment lines represent  $\pi$ -bonds between  $p_x$  orbitals. Pairs of orbitals containing one electron (denoted by a dot) form covalent electron-pair bonds. Orbitals containing two electrons (i.e., two dots) are lone pairs

and are non-bonding. Note that in the monomer on the right of (b) that a triple bond (two  $\pi$ -bonds and a  $\sigma$ -bond) resembling the bonding of the  $N_2$  molecule is found.

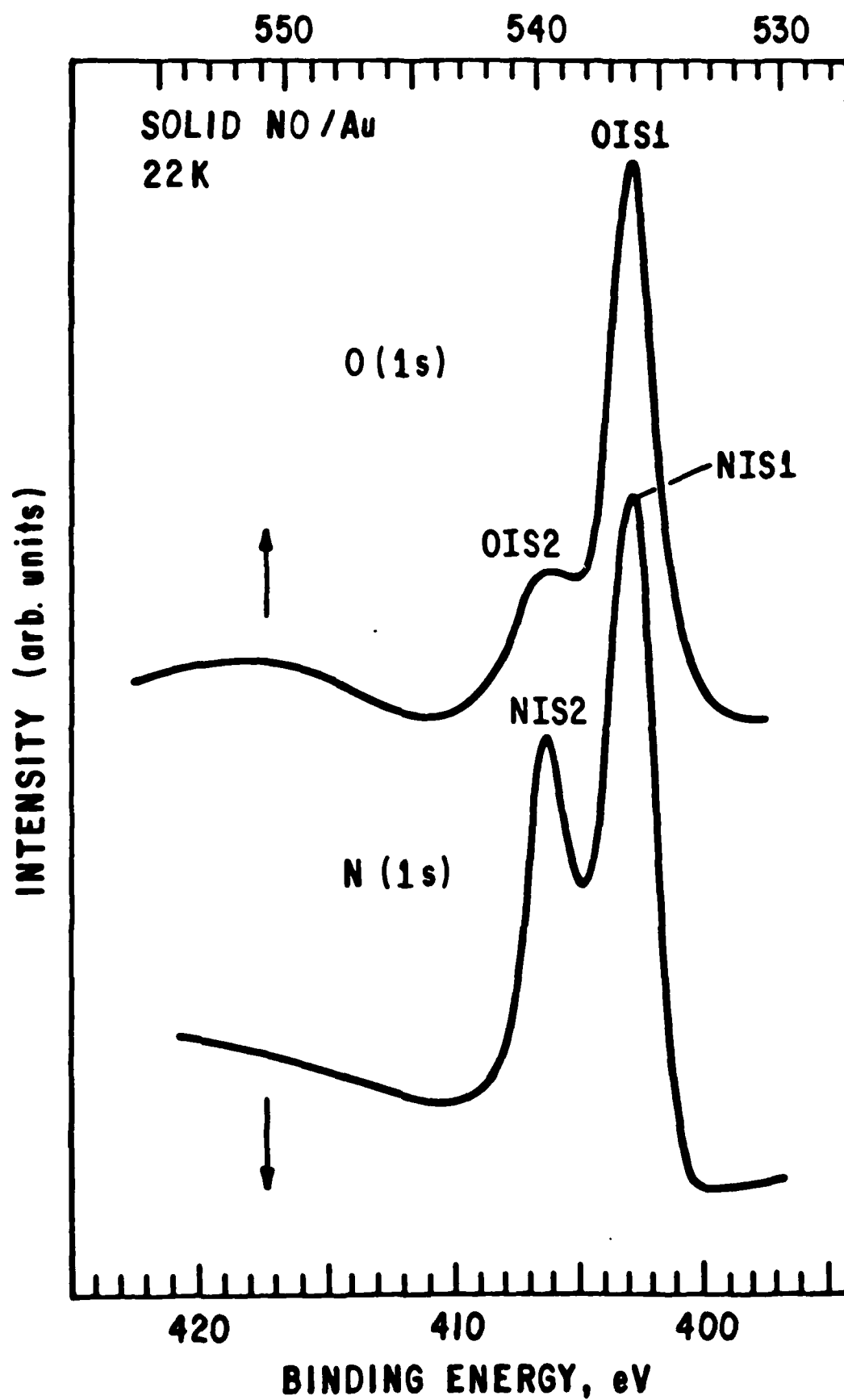


Fig. 1b

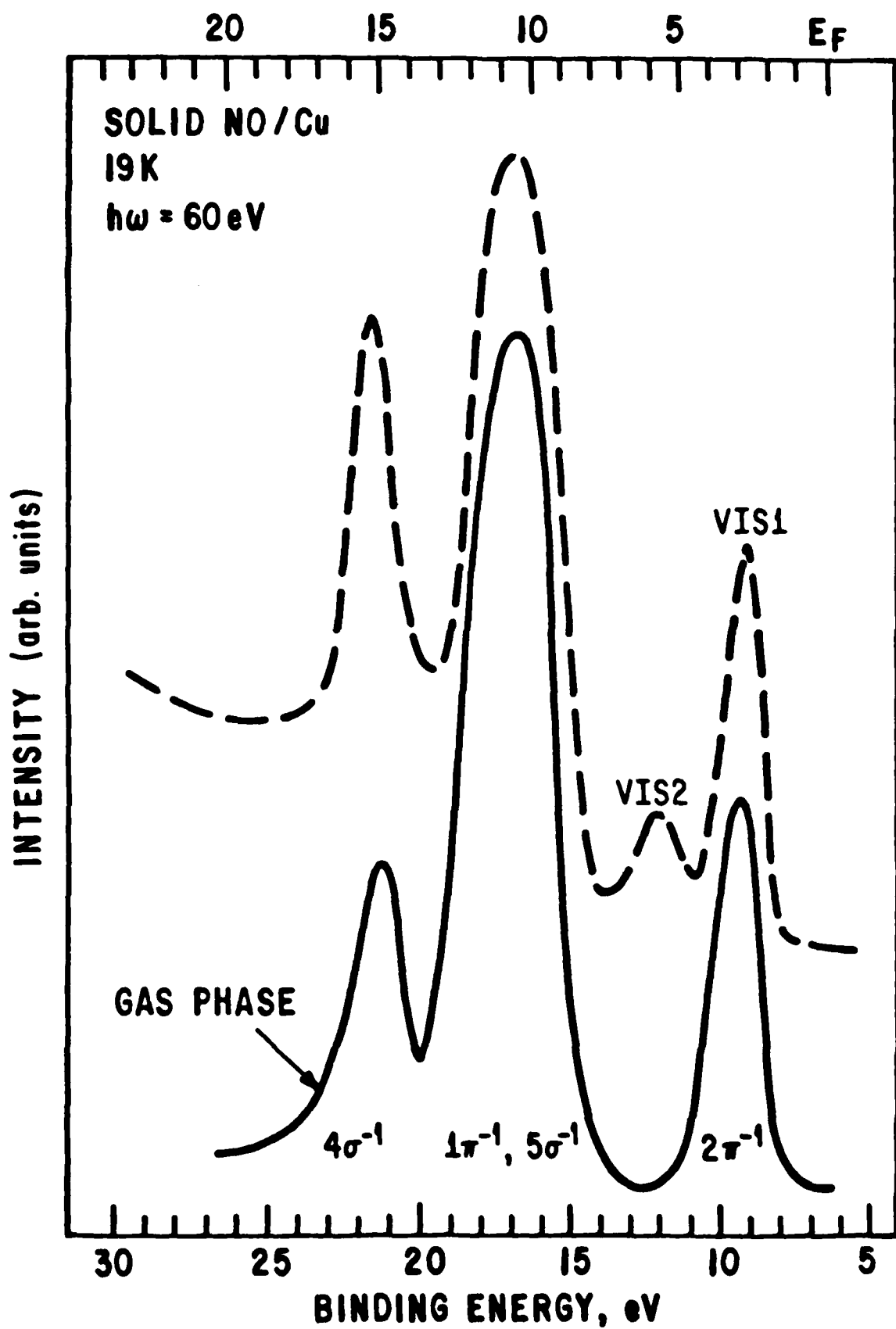


Fig. 1a

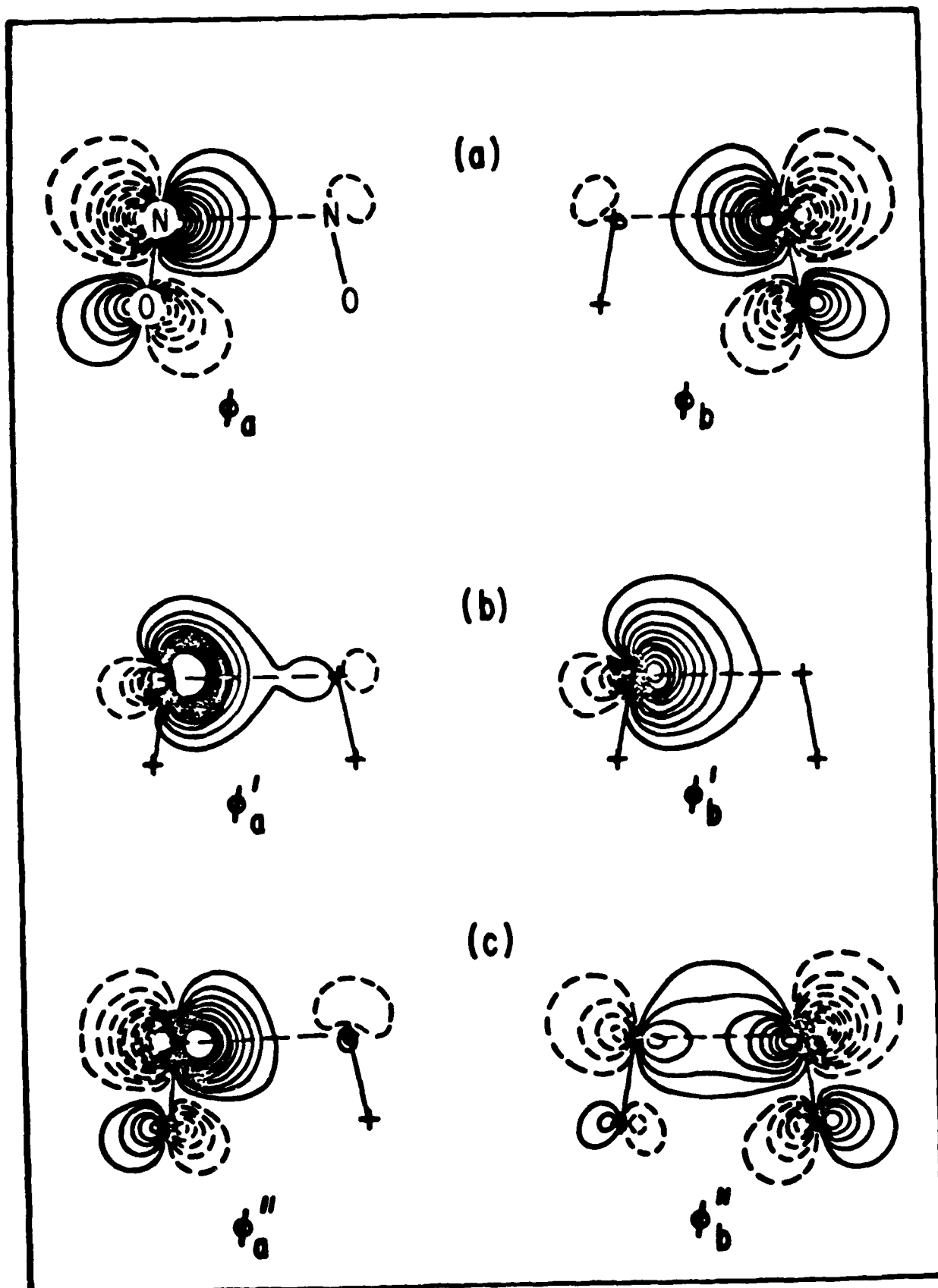
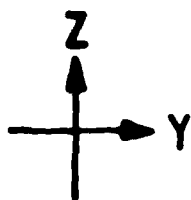
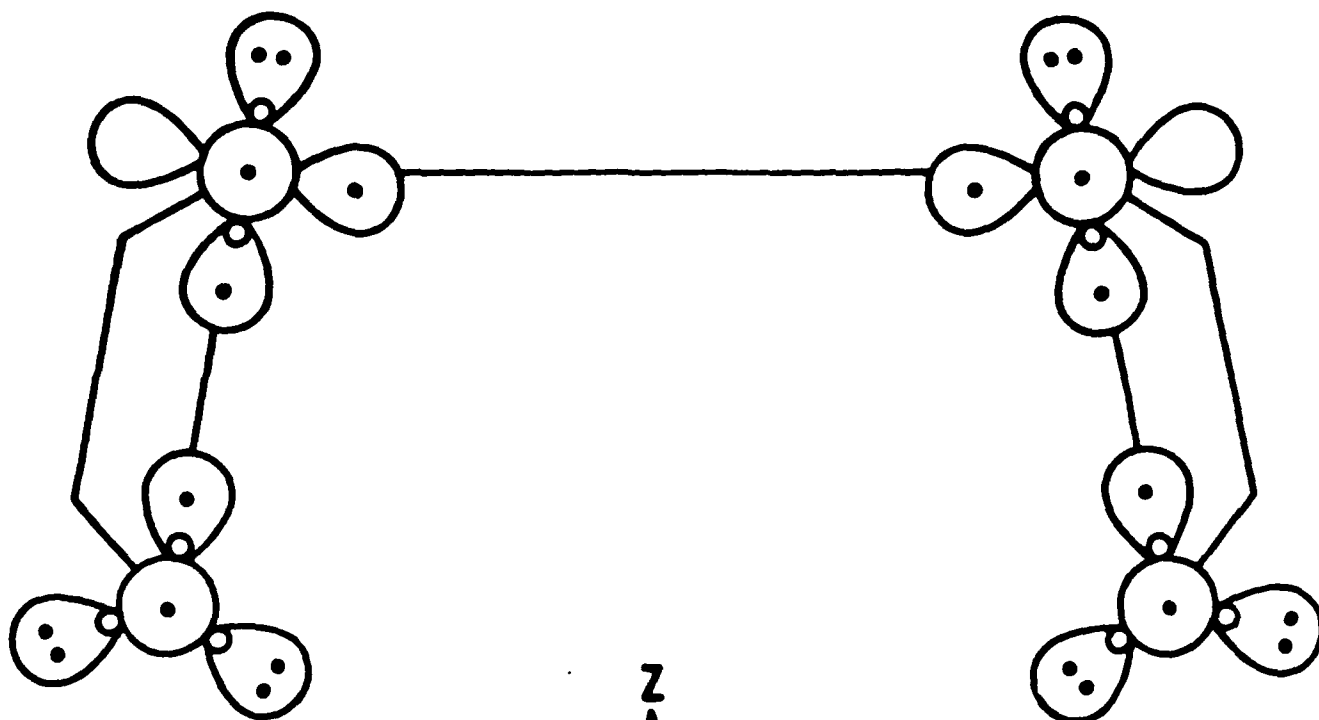


Fig. 2

(a)



(b)

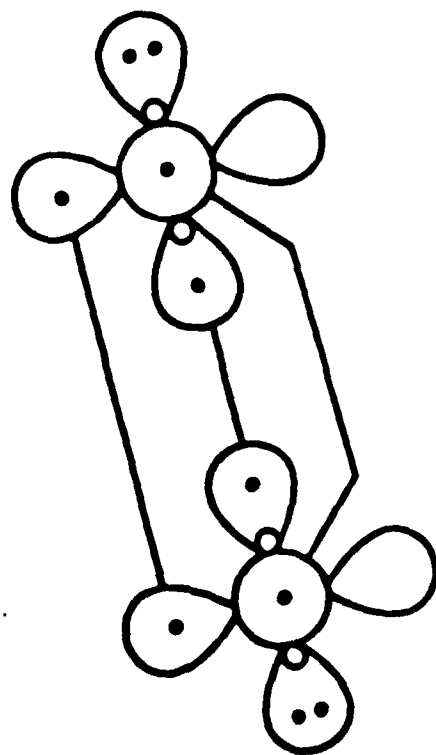
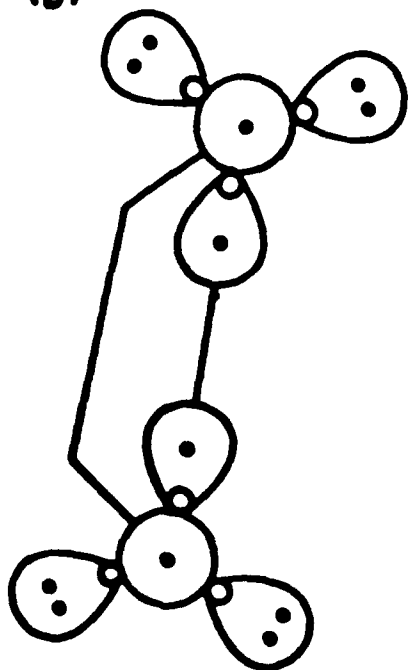


Fig. 2

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